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The Kinetics of Ligand Substitution in Bis(*N*-alkylsalicylaldiminato)nickel(II) Complexes: a Study on the Reactivity of Square-planar *versus* Octahedral Coordination

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Abstract

The bis(*N*-alkylsalicylaldiminato)nickel(II) complexes Ni(R-sal)$_2$ with R = $-CH(CH_2-OH)-CH(OH)-Ph$ (**I**), R = $-CH(CH_3)-CH(OH)-Ph$ (**II**) and R = $-CH_2-CH_2-Ph$ (**III**; Ph = phenyl) were prepared and characterized. In the solid state **I** and **II** are paramagnetic (μ = 3.2 and 3.3 BM at 20 °C, respectively), whereas **III** is diamagnetic. It follows from the UV–Vis spectra that in acetone solution **I** is six-coordinate octahedral and **III** is four-coordinate planar, the spectrum of **II** showing characteristics of both modes of coordination. Vis spectrophotometry and stopped-flow spectrophotometry were applied to study the kinetics of ligand substitution in **I**–**III** by H$_2$salen (= *N*,*N'*-disalicylidene-ethylenediamine) in the solvent acetone at different temperatures. The kinetics follow a second-order rate law, rate = k[H$_2$salen][complex]. At 20 °C the sequence of rate constants is k(III):k(II):k(I) = 11 850:40.6:1. The activation parameters are $\Delta H^{\ddagger}(I) = 112$, $\Delta H^{\ddagger}(II) = 40.7$, $\Delta H^{\ddagger}(III) = 35.7$ kJ mol^{-1} and $\Delta S^{\ddagger}(I) = 92$, $\Delta S^{\ddagger}(II) = -103$, $\Delta S^{\ddagger}(III) = -89$ J K^{-1} mol^{-1}. The enormous difference in rate between complexes **I**, **II** and **III**, which is less pronounced in methanol, is attributed to the existence of a fast equilibrium planar ⇌ octahedral, which is established in the case of **I** and **II** by intramolecular octahedral coordination through the hydroxyl groups present in the organic group R. An A-mechanism is suggested to control the substitution in the sense that the entering ligand attacks the four-coordinate planar complex, the octahedral complex being kinetically inert.

Introduction

We have shown recently [1] that the ligand substitution in square-planar bis(*N*-alkylsalicylaldiminato)nickel(II) complexes Ni(R-sal)$_2$ as carried out in acetone according to eqn. (1)

$$Ni(R\text{-}sal)_2 + H_2salen \longrightarrow Ni(salen) + 2R\text{-}salH \qquad (1)$$

follows rate law (2)

$$\text{rate} = k_{obs}[Ni(R\text{-}sal)_2] = k[H_2salen][Ni(R\text{-}sal)_2] \qquad (2)$$

(H$_2$salen = *N*,*N'*-disalicylidene-ethylenediamine)

The mechanism of eqn. (1) is associative in the sense that the rate-controlling step is the bimolecular reaction of the complex with the entering ligand via the 'adduct' [Ni(R-sal)$_2$, H$_2$salen] formed in a fast pre-equilibrium [1].

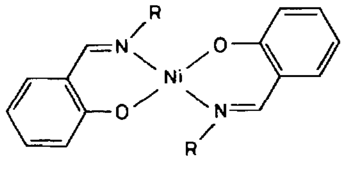
The addition of nucleophiles such as pyridine (= py) to complexes Ni(R-sal)$_2$ establishes the following equilibria [1, 2]

$$Ni(R\text{-}sal)_2 + 2py \overset{K_1}{\rightleftharpoons} Ni(R\text{-}sal)_2(py)$$
$$+ py \overset{K_2}{\rightleftharpoons} Ni(R\text{-}sal)_2(py)_2 \qquad (3)$$

It was shown convincingly [1] that in the presence of pyridine reaction (1) takes place exclusively via the four-coordinate species Ni(R-sal)$_2$, the adducts Ni(R-sal)$_2$(py) and Ni(R-sal)$_2$(py)$_2$ being kinetically inert. The net result is that the rate of eqn. (1) is reduced considerably by the addition of pyridine.

To shed more light on this question of reactivity of four-coordinate nickel(II) complexes as compared to five-coordinate and to six-coordinate octahedral ones, reaction (1) was studied with the complexes Ni(R-sal)$_2$ = **I**, **II** and **III**.

Ni(R-sal)$_2$ =



I: R = $-CH(CH_2-OH)-CH(OH)-Ph$
II: R = $-CH(CH_3)-CH(OH)-Ph$
III: R = $-CH_2-CH_2-Ph$

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Complex **III** is expected to be four-coordinate with a planar *trans*-N_2O_2 coordination geometry [3], whereas **I** and **II** could be six-coordinate with a distorted octahedral N_2O_4 coordination geometry in an either meridional or facial arrangement.

Experimental

Materials

The amines 2-phenylethylamine (Aldrich), (1*S*, 2*S*)-(+)-2-amino-1-phenyl-1,3-propandiol (Aldrich) and L-norephedrine (= (1*R*,2*S*)-(−)-2-amino-1-phenyl-1-propanol); Fluka) were commercially available. The ligand H_2salen was prepared as described earlier [1]. The solvents acetone and methanol were reagent grade (Merck).

Preparation of the Complexes

Complexes **I**–**III** were prepared from Ni(sal)$_2$·2H_2O (= bis(salicylaldehydato)nickel(II) dihydrate) [4] and the corresponding amine R-NH_2 according to the following general procedure. 5 mmol of Ni(sal)$_2$·2H_2O were suspended in 50 ml $CHCl_3$ under stirring and 11 mmol R-NH_2 were added. Upon heating the solid Ni(sal)$_2$·2H_2O dissolved by reacting with the amine. After filtration of the hot solution and cooling of the filtrate the complex Ni(R-sal)$_2$ crystallized. It was filtered, washed with cold $CHCl_3$ and dried over P_4O_{10}.

In the case of **II** the solvent EtOH was used instead of $CHCl_3$, crystallization was initiated by addition of Et_2O to the solution and the crystals were washed with Et_2O. In the case of **III** crystallization was achieved by adding petroleum ether (boiling point 40–80 °C) to the chloroform solution of the complex.

III was recrystallized twice from $CHCl_3$ (green small needles; melting point (m.p.) 202 °C). Complexes **I** and **II**, which could not be recrystallized, were obtained as hydrates Ni(R-sal)$_2$·$x$$H_2O$ ($x \approx 6$). Drying *in vacuo* over P_4O_{10} for *ca.* 14 h at 115 °C (**I**) or 70 °C (**II**) lead to anhydrous **I** (light green powder; m.p. 248–250 °C) and monohydrate **II**·H_2O (yellow brown powder; m.p. 125 °C).

Anal. of **I**; Found: C, 63.70; H, 5.36; N, 4.59; Ni, 9.71. Calc. for $C_{32}H_{32}N_2NiO_6$: C, 64.13; H, 5.38; N, 4.67; Ni, 9.80%.

Anal. of **II**·H_2O; Found: C, 65.17; H, 6.12; N, 4.82; Ni, 10.27. Calc. for $C_{32}H_{34}N_2NiO_5$: C, 65.66; H, 5.86; N, 4.79; Ni, 10.03%.

Anal. of **III**: Found: C, 70.92; H, 5.44; N, 5.45; Ni, 11.42. Calc. for $C_{30}H_{28}N_2NiO_2$: C, 71.03; H, 5.56; N, 5.52; Ni, 11.57%.

UV–Vis Spectra

The absorption spectra were taken on a diode array spectrophotometer (Hewlett-Packard; 8451A) and on a double beam spectrophotometer (Zeiss; DMR 22). The pathlength of the cell was 1 cm and the concentrations were 5×10^{-3} M ($\lambda > 500$ nm) and 5×10^{-4} M ($\lambda < 500$ nm) for **I** and **II**. Due to low solubility the concentration of **III** was 10^{-4} M.

Magnetic Measurements

The magnetic moments were determined on a magnetic susceptibility balance (Johnson Matthey) at 20 °C.

Kinetic Measurements

Ligand substitution in **I** according to eqn. (1) was followed on the HP spectrophotometer (see above) in 1 cm double chamber cells. Solutions of the complex (2×10^{-4} M) and of the ligand H_2salen (2×10^{-3}–2×10^{-2} M) in acetone were filled into the chambers of the cell and thermostated. At $t = 0$ the solutions were mixed by shaking and the increase in absorbance A was followed at 415 nm at constant time intervals. Rate constants were obtained by fitting an exponential function to the A/t data points with a computer program based on the least-squares method (deviation from ideal first-order kinetics $\leqslant 1\%$).

Ligand substitution in **II** and **III** was followed with a modified [5] Durrum stopped-flow spectrophotometer connected to a transient recorder. As for the slow reaction of **I**, conditions for **II** and **III** were pseudo-first-order ([H_2salen] $\geqslant$ 10[complex]) and the reactions were monitored at 450 (**II**) and 475 (**III**) nm, respectively.

Results and Discussion

Absorption Spectra and Magnetic Data

The acetone spectra shown in Fig. 1 clearly show a rather different absorption behaviour of complexes **I**, **II** and **III**. Complex **I** produces a three band spectrum with a very strong absorption at 368 nm and two weak bands at 592 and 960 nm, respectively (see Table I). In contrast to **I**, complex **III** has its strongest absorption at 416 nm and a relatively weak one at 616 nm (see Table I). One has to take into account that the organic group R = –$(CH_2)_2$–Ph in complex **III** is a non-coordinating one and that the similar complex Ni(Et-sal)$_2$ is diamagnetic with a planar *trans*-N_2O_2 arrangement of the donor atoms, as shown by X-ray analysis [3]. Taking this into consideration one has to interpret the acetone spectrum of **III** as being indicative of a planar four-coordinate nickel(II) complex. The fact that in methanol complex **III** gives a very different spectrum (see Table I) with a strong absorption at 368 nm ($\epsilon = 5100$ M^{-1} cm^{-1}) and two weak absorptions* at higher wave-

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*The solubility of **III** in methanol is unfortunately limited to approx. 1×10^{-4} M so that the two weak absorptions at approx. 600 and 975 nm could not be characterized accurately.

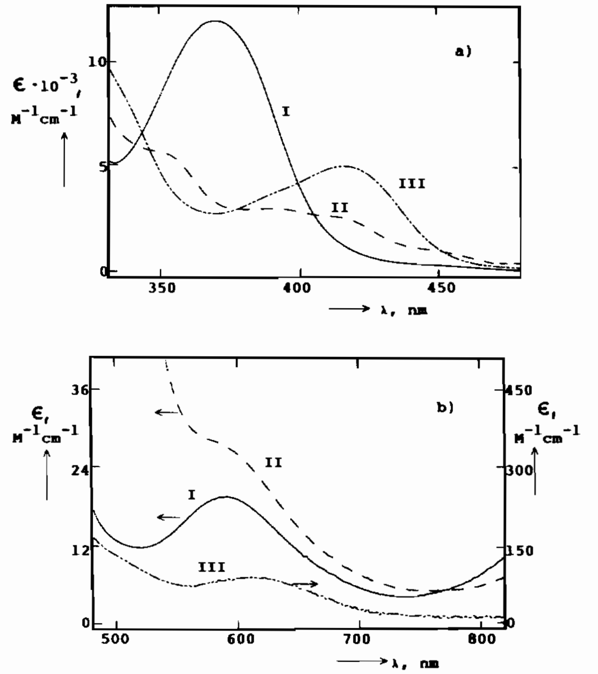


Fig. 1. Absorption spectra for complexes I–III in acetone in the range 330–480 nm (a) and 480–820 nm (b).

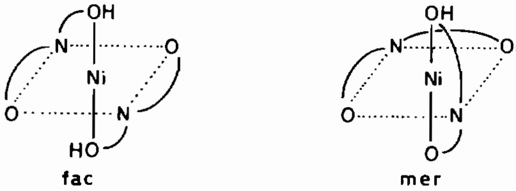
TABLE I. Absorption Data for Complexes I, II and III in Acetone and Methanol in the Range 350–1200 nm

Complex	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))
Solvent acetone	
I	368 (12000); 592 (20); 960 (20)
II	≈ 350 sh (≈ 5700); ≈ 415 sh (≈ 2700); ≈ 590 sh (≈ 28); 975 (14)
III	416 (5100); 616 (95)
Solvent methanol	
I	367 (11670); 603 (17); 975 (20)
II	367 (8930); 603 (14); 975 (20)
III[a]	368 (5100); ≈ 600 (≈ 40)

[a] The solubility of III in methanol is unfortunately limited to approx. 1 × 10^{-4} M; the weak absorptions at approx. 600 and 975 nm could not be characterized accurately, therefore.

length suggests that in methanol most of the planar four-coordinate complex III is converted into its octahedral adduct, III·$(MeOH)_2$**. This would mean on the other hand that the spectrum of I in acetone (with its three absorptions at exactly the same wavelengths as complex III in methanol) reflects octahedral coordination as produced by internal coordination of the hydroxyl groups being present in the organic group R = $-CH(CH_2-OH)-CH(OH)-Ph$ of complex I.

The acetone spectrum of complex II finally lies somewhat in between those of I and III (see Fig. 1 and Table I), which could mean that octahedral coordination in II according to (4) is weaker in this case so that in acetone solution there is an equilibrium II(octahedral) ⇌ II(planar). The spectrum of II in acetone is, hence, a superposition of the spectra of a planar and octahedral complex.



(4)

The absorption spectra of complexes I–III in methanol (see Table I) are very interesting in a twofold sense. Firstly, all three of them show one strong absorption at 367–368 nm and two weak ones at 603 and 975 nm, respectively. This means that in methanol all three complexes are coordinated in an octahedral fashion. Secondly, the absorption coefficient ϵ at λ_{max} = 367 nm is highest for I and lowest for III. This could indicate that octahedral coordination by methanol is facilitated and intensified by hydrogen bonding between the coordinated methanol and the hydroxyl groups present in the organic groups attached to the nitrogen donor atoms of I and II. Since I offers four hydroxyl groups, II only two and III none, the intensity of absorption drops correspondingly.

This interpretation of the spectra is supported by the magnetic data which were obtained for the solid complexes I–III at 20 °C. I: μ_{exp} = 3.2 BM; II: μ_{exp} = 3.3 BM; III: diamagnetic. In the solid state the hydroxyl groups present in the organic groups attached to the nitrogen atoms of I and II are obviously coordinated to the nickel to produce octahedral coordination in an either intramolecular or intermolecular fashion. Complex III lacks these hydroxyl groups and is, therefore, left with a planar *trans*-N_2O_2 coordination leading to diamagnetism.

Kinetic Studies

The study of reaction (1) at different excess concentrations of H_2salen leads to absorbance/time data which fit to one exponential function very satisfactorily. The values of the experimental rate constants k_{obs} resulting from this fitting increase linearly with [H_2salen]. Figure 2 presents the data obtained for complex III at 20 °C as an example. From the slope

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**A spectrophotometric titration of the complex Ni(R-sal)$_2$ (R = $-(CH_2)_4-Ph$) with MeOH in acetone at 25 °C yields an equilibrium constant β_2 = (6 ± 3) × 10^{-3} M^{-2} for the reaction Ni(R-sal)$_2$ + 2MeOH ⇌ Ni(R-sal)$_2$(MeOH)$_2$ [6]. This number would predict 80–90% conversion of Ni(R-sal)$_2$ to Ni(R-sal)$_2$(MeOH)$_2$ for pure methanol as solvent.

TABLE II. Rate Constants (k) and Activation Parameters for Reaction (1) in Acetone^a and Constant $K_{p,o}$ for Equilibrium (6)

Complex	Temperature (K)	k^b (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$K_{p,o}{}^c$
I	293	0.00476 ± 0.00022	112 ± 3.0	92 ± 11	11850
	301	0.0148 ± 0.0010			5070
	309	0.0748 ± 0.0033			2510
	318	0.190 ± 0.012			1000
II	293	1.39 ± 0.023	40.7 ± 3.0	−103 ± 10	39.6
	301	1.88 ± 0.11			39.0
	309	3.08 ± 0.22			38.0
	318	5.50 ± 0.29			33.4
III	293	56.4 ± 1.6	35.7 ± 2.8	−89 ± 10	
	301	75.1 ± 1.0			
	309	120 ± 6.0			
	318	189 ± 2.0			

^{a}At [complex] = 1×10^{-4} M. ^{b}Calculated by least-squares fitting of the function $k_{obs} = k[H_2salen]$ to the data obtained for k_{obs} at $[H_2salen]$ = 0.001, 0.004, 0.006, 0.008 and 0.01 M (see Fig. 2). ^{c}Obtained from the relationship $K_{p,o} = (k(III)/k) - 1$ (see equation (8)).

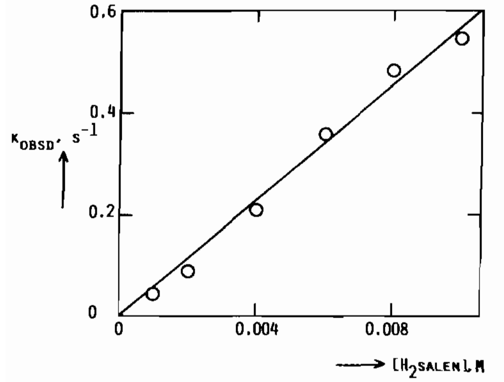


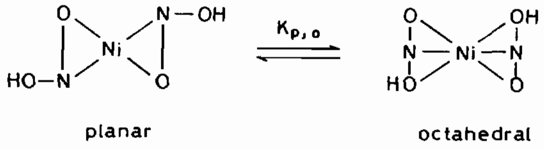
Fig. 2. Plot of rate constant k_{obs} *vs.* concentration of the incoming ligand H_2salen for complex III ([complex] = 1×10^{-4} M; solvent acetone; 20 °C.

of the straight line in Fig. 2 rate constant k is obtained (see Table II).

The results prove that ligand substitution according to eqn. (1) follows rate law (2). The rate of substitution in complexes **I**, **II**, and **III** is very different, however. At 20 °C the relative rates are found to be

$$k(III):k(II):k(I) = 11\,850:40.6:1 \qquad (5)$$

To explain this enormous difference in rate one has to consider the following findings: (i) the rate of ligand substitution in the planar complex Ni(n-Pr-sal)$_2$ (n-Pr = n-propyl) is drastically reduced by the addition of pyridine, *i.e.* by converting the planar complex into an octahedral one [1], and (ii) the rate of substitution in the system Ni(n-Pr-sal)$_2$/py/acetone can be quantitatively correlated to the fraction of the planar, four-coordinate complex present [1]. It is reasonable, therefore, to attribute the reduced rate of complexes **I** and **II** to the existence of equilibrium (6)



(6)

It has been shown by relaxation techniques that equilibration according to (6) is a very fast process [7]. This would mean that (6) is a pre-equilibrium, which does not control the rate. If only the planar, four-coordinate species reacts with H_2salen (present in excess) in a second-order step (rate constant k_p), eqn. (7) applies

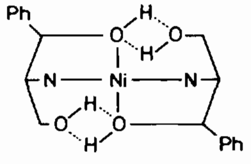
$$\text{rate} = k_p(1 + K_{p,o})^{-1}[H_2salen][complex]_{tot} \qquad (7)$$

Since complex **III** is not subject to equilibrium (6) one can set $k(III) \equiv k_p$ and assume that the planar forms of **I** and **II** react with rate constant $k(III) \equiv k_p$. This allows the calculation of the equilibrium constant $K_{p,o}$ on the basis of relationship (8) from

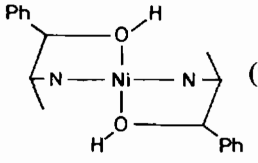
$$k = k_p/(1 + K_{p,o}) \equiv k(III)/(1 + K_{p,o}) \qquad (8)$$

the data for k(I) and k(II) (see Table II).

The numbers obtained for $K_{p,o}$ at 20 °C are surprisingly different, namely 11 850 for **I** and 39.6 for **II**. Since both **I** and **II** can provide hydroxyl groups for intramolecular octahedral coordination, one could argue that the second hydroxyl group present in **I** is the better donor than the group $-CH(CH_3)-CH(OH)-Ph$ present in both **I** and **II**. This argument is not very convincing, however, and a more reasonable explanation results from the fact that in **I** the group attached to the donor nitrogen in **I** offers two hydroxyl groups and in the case of **II** only one. Looking at molecular models of **I** and **II** one recognizes that the exceptional kinetic inertness of **I** could be due to an additional stabilization of octahedral **I** by internal hydrogen bonding as shown schematically in (9) (coordination by phenolic oxygen omitted)



I



II

(9)

One has to keep in mind, additionally, that the calculation of $K_{p,o}$ from k according to eqn. (8) (with $k_p \equiv k(\text{III})$) is a rather formal procedure which ascribes the reduced reactivity of **I** and **II** as compared to **III** exclusively to internal octahedral coordination. Another factor that could make complexes **I** and **II** less reactive is oligomerization in solution via the hydroxyl groups.

The activation parameters obtained from the temperature dependence of k reflect the following trends (see Table II): (i) for the planar complex **III** the smallest activation enthalpy $\Delta H^{\ddagger}$ of 35.7 kJ mol^{-1} is found and a negative activation entropy of -89 J K^{-1} mol^{-1}, which is in line with a bimolecular rate-controlling step, *i.e.* the nucleophilic attack of H_2salen on **III**; (ii) complex **I** is highest in $\Delta H^{\ddagger}$ (112 kJ mol^{-1}) and positive in $\Delta S^{\ddagger}$ (+92 J K^{-1} mol^{-1}), whereas the corresponding data for **II** are closer to the data obtained for **III**. Since the equilibrium constant $K_{p,o}$ is calculated on the basis of the assumption $k(\text{III}) \equiv k_p$ according to eqn. (8), the values for the enthalpy and entropy of reaction (6) for complexes **I** and **II** have to result from the differences $\Delta H^{\ddagger}(\text{III}) - \Delta H^{\ddagger}$ and $\Delta S^{\ddagger}(\text{III}) - \Delta S^{\ddagger}$, since $K_{o,p} \gg 1$. One finds $\Delta H_{p,o}(\text{I}) = -76.3$ and $\Delta H_{p,o}(\text{II}) = -5$ kJ mol^{-1} and $\Delta S_{p,o}(\text{I}) = -181$ and $\Delta S_{p,o}(\text{II}) = 14$ J K^{-1} mol^{-1}. This means that the observed increase in the activation enthalpy $\Delta H^{\ddagger}$ for reaction (1) upon going from complex **III** to **I** is due to more energy having to be provided to convert the octahedral complex to the four-coordinate planar (or five-coordinate) one.

The spectrum of **II** in acetone (see Fig. 1) was taken at 20 °C. At this temperature the calculation of $K_{p,o}$ for **II** leads to 39.6 (see Table II) which would mean that a fraction of approx. 97% of **II** should be present with an octahedral coordination. The spectrum of **II** indicates that this fraction is obviously smaller. This again shows that the calculation of $K_{p,o}$ according to eqn. (8) is a very formal procedure which does not take into account additional rate-effecting factors (such as steric hindrance, for example).

The importance of internal octahedral coordination in complexes **I** and **II** as rate reducing factor in ligand substitution according to (1) is also reflected by the results of some preliminary studies on reaction (1) as carried out in methanol instead of acetone. The absorption spectra taken in methanol prove (see Table I) that all three complexes form more or less stable octahedral adducts with methanol. As a matter of fact, the enormous difference in rate observed in acetone (see sequence (5) for example) is greatly reduced in methanol. At [complex] = 1×10^{-4} M and [H_2salen] = 1×10^{-3} M the relative experimental rate constants k_{obs} for the solvent methanol are (20 °C): $k_{obs}(\text{III}) : k_{obs}(\text{II}) : k_{obs}(\text{I}) = 30:2.2:1$.

This means that the rate reducing internal octahedral coordination in **I** and **II** occurring in acetone is replaced by adduct formation with methanol in this latter solvent, the methanol adducts of **I** and **II** being more stable (*i.e.*, less reactive) though than the one formed by **III** (an explanation for this different stability is given in the discussion of the spectra; see above). The interesting fact that at 20 °C k_{obs}(III in MeOH) is by a factor of 5.6 greater than k_{obs}(III in acetone) is probably due to a larger rate contribution of a solvent-initiated reaction channel k_s in the more polar and protic solvent methanol according to a two-term rate law, rate = $(k_s + k[H_2\text{salen}])[\text{complex}]$.

Conclusions

The findings of the present contribution support earlier results [1] in the general sense that the rate of ligand substitution in complexes Ni(R-sal)$_2$, in which the group R possesses donor capacity and which are therefore subject to an intramolecular coordination equilibrium planar $\rightleftharpoons$ octahedral, can be interpreted as being controlled by the fraction of the four-coordinate planar complex (or five-coordinate complex) present. The octahedral complex appears to be kinetically inert. This behaviour is in line with the operation of an A-mechanim, the four-coordinate planar complex (or the five-coordinate complex) being a much better acceptor for the entering nucleophile than the octahedral complex.

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